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SURFACE STRUCTURE AND PROPERTIES OF
CHROMIUM NEEDLE CRYSTALS

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ABSTRACT

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The surface structure and tensile strength of filamentary chromium crystals (whiskers) prepared by condensation from the vapor phase in vacuum have been investigated. It was found that the surface of such crystals has growth steps with a height of approximately 2000 \AA . The tensile strength of the crystals depends on their cross section and attains values of 590 kg/mm^2 , even for crystals exhibiting macroscopic growth steps. The growth mechanism of acicular crystals (needles) obtained from the vapor phase is discussed.

INTRODUCTION

Author ↑

Filamentary crystals of metals (metal whiskers) are usually prepared by reduction or decomposition of the appropriate salts. A less common method of growing crystals is to condense them from the vapor phase; this method has been tested primarily with metals whose vapor phase is readily obtained (refs. 1 and 2).

Filamentary chromium crystals were investigated in references 3 to 5. By anodic dissolution of chromium-bearing alloys, Webb and Forgeng (ref. 5) obtained chromium needles from 1 to 3 microns in diameter and 1 mm in length. Bending strength tests of these crystals yielded values of about 800 kg/mm^2 . Morelock (ref. 3) observed the growth of whiskers from the vapor phase in vacuum.

Numbers in the margin indicate pagination in the original foreign text.

Acicular chromium crystals have also been grown by vapor condensation on a surface with a temperature gradient (ref. 4). The crystals had a cross section of $3\cdot 5\cdot 10^{-6}$ to $1\cdot 10^{-2}$ mm² and a length of from 10 to 15 mm. Since the term filamentary or whisker crystal is usually applied only to extremely perfect, very strong samples and the crystals obtained often did not satisfy these conditions, it was decided to call them acicular, or needle, crystals. This concept refers only to the shape of crystals having a considerable length in one direction, regardless of the structure and properties of the samples. It is applied to filamentary crystals, or whiskers, in particular. This paper deals with an investigation of the surface structure and the characteristic mechanical properties of chromium needles; also discussed is the mechanism of formation of needle crystals by condensation.

EXPERIMENTAL RESULTS

Surface Structure of Needle Crystals

The surface of needle crystals formed by condensation from the vapor phase (ref. 4) was studied with an MIM-8 optical microscope and an EM-3 electron microscope (using the shadow method).

It was found that the surface of the needle crystals is not even and that their cross section varies over the length of the crystal. Usually the crystals taper down from their base to the top; only the regions close to the thin end exhibit a relatively even surface. On the rest of the surface, macroscopic growth steps can be observed, forming a ladder structure. The average height 893 of the individual steps is 1700 to 2300 Å.

The growth steps move from the base of the crystal to its top and rarely form closed regions on the side faces (fig. 1). The growth structures on neighboring faces are not related with each other but develop independently.

A remarkable feature on the crystal surface is the presence of two steps in the form of two regular concentric circles (in fig. 1, they are situated at the intersection of the two lines indicated by arrows); their nature is not yet quite clear.

The surface structure of the different faces of one crystal is not always uniform. There are samples with one of their faces relatively smooth, having only growth steps of a regular geometrical form and with the other faces rough (fig. 2).

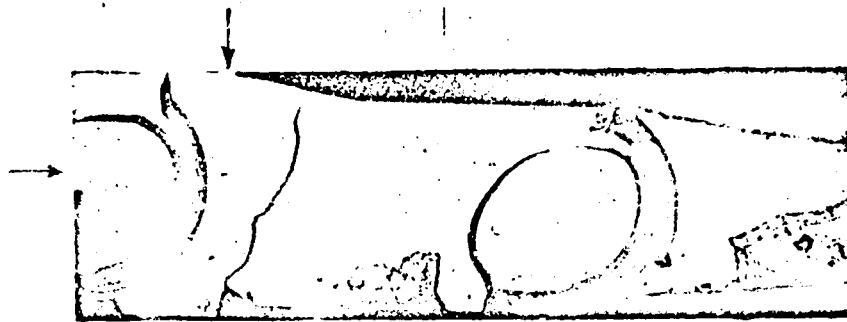


Figure 1. Photomicrograph of a Surface Region on One Face of a Chromium Needle. X240

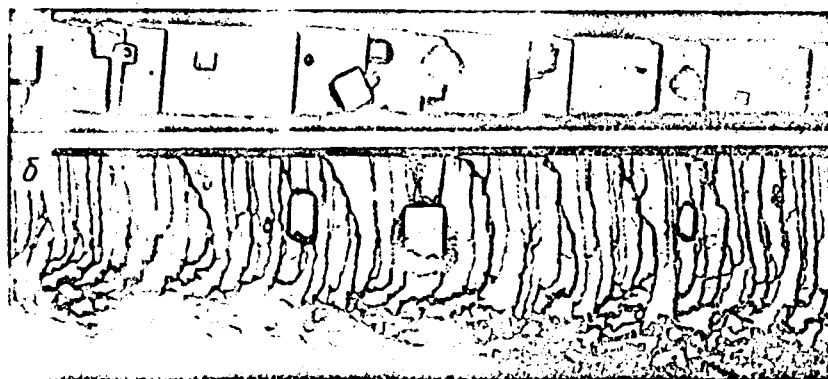


Figure 2. Photomicrograph of Surface Regions on Two Faces (a, b) of One Chromium Needle. X200

Sometimes a uniform step-laminated, or terraced, structure can be observed over the entire surface (fig. 3). The cross section of the majority of needle crystals is in the shape of rectangles, squares, and rectangular trapezoids.

Electron-microscopic studies confirm the fact that, in addition to surface regions, steplike (fig. 4a) and complex profiles (fig. 4b) occur. The height estimates of the individual steps obtained from electron-microscopic studies agree with the results of the optical measurements. Some steps have a rather 1894 irregular fine structure (fig. 4).

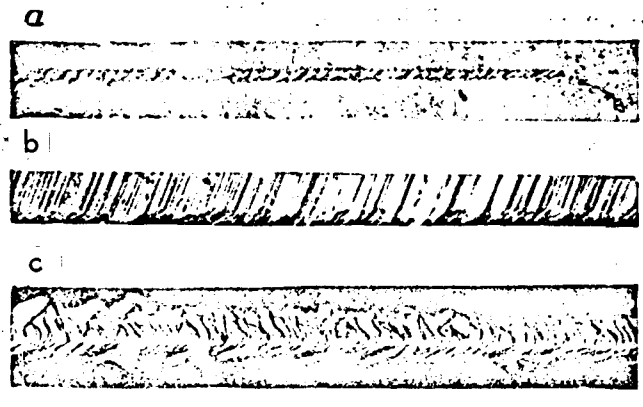


Figure 3. Typical Step-laminated Structure of Needle Crystals. X500

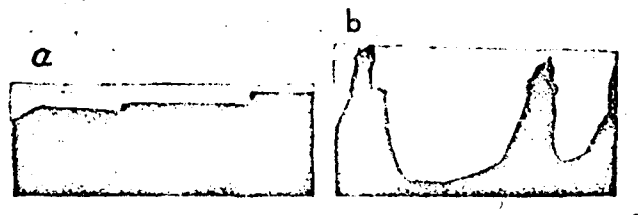


Figure 4. Electron-microscopic Photographs of Two Different Chromium Crystals. X800

Tensile Strength of Chromium Needles

The tensile strength of the crystals was determined by tensile testing according to the procedure outlined in reference 6. Preliminary investigations (ref. 7) have shown that a scatter in the results occurs even with samples of uniform cross section; this scatter is rather essential in the case of relatively thick crystals with an imperfect surface structure. The tensile strength of the crystals increases with decreasing crystal cross section.

Our work deals with the tensile strength of thin needle crystals with a cross section of less than $20 \cdot 10^{-6} \text{ mm}^2$. The results of the tests are listed in the table.

TABLE
TENSILE STRENGTH OF CHROMIUM NEEDLES

Sample No:	1	2	3	4	5			6					7
Number of tests	1	1	1	1	1	2	3	1	2	3	4	5	1
Cross section $S \cdot 10^{-6}$, mm^2	19	12	9	7	4.5	4.5	4.5	1.2	3.1	3.3	3.8	4	1.4
Tensile strength σ , kg/mm^2	250	190	260	245	160	310	260	410	320	380	350	400	590

It must be emphasized that the crystals were selected for testing according to their size without setting any pre-conditions of their surface state. Since all the crystals investigated were sufficiently thin, they had a relatively 895 even surface with growth steps.

The directional dependence of the tensile strength was not investigated. Rupture of the crystals took place without any appreciable prior plastic

deformation, due to fracture in the cleavage plane. In some cases a plastic deformation was observed to be localized near the rupture site; the plane of fracture and the tension axis formed an angle of 45° . Some samples (see table) were subjected to repeated tensile tests; after each test the strength of the remaining piece of the sample was investigated. Besides the normally observed increase in strength of the remainder, in some cases a decrease in strength was found when the samples were tested repeatedly. However, this might be attributed to deformation of the samples when prepared for testing. The fracture of crystals which were not uniform in cross section happened in most cases in the middle section of the samples and not in the minimum cross section (near the point where the sample was clamped).

Discussion of the Results

The growth mechanism of filamentary crystals condensed from the vapor phase is, according to Sears (ref. 1), based on the assumption that the formation of similar crystals will be observed only at certain supersaturation values α , below some critical value α_{cr} . For $\alpha > \alpha_{cr}$, the nuclei of molecular layers appear on the side surfaces, and a radial growth takes place with formation of three dimensional crystals. The value of α_{cr} can be determined from the expression

$$\ln \alpha = \frac{\pi a \sigma^2 M}{\rho k T^2 R \ln \frac{B}{N}}, \quad (1)$$

where a is the distance between crystal planes, σ is the surface energy, M is the molecular weight, ρ is the density of the crystallizing substance, T is the crystallization temperature, N is the number of nuclei (seeds) formed per unit

time per unit area, k is the Boltzmann constant, R is the universal gas constant, $B \approx 10^{20}$.

There exists however a series of experimental observations which can hardly be explained by the assumption of filamentary crystals growing at low supersaturations. This question has already been discussed in the literature (refs. 8 and 9).

In Sears' own experimental work (ref. 1) there are some discrepancies with the theory. For example, he believes that the experimentally obtained value of α_{cr} for Ag whiskers ($\alpha = 10$) is in good agreement with the one predicted by theory ($\alpha = 4$). Actually, according to our calculations, an N -value of approximately nucleus/cm²·sec corresponds to $\alpha = 4$, and for $\alpha = 10$ we obtain $N \approx 10^8$ nuclei/cm²·sec.

An analogous rough calculation was carried out on the basis of the data of the authors of references 4 and 7 for chromium needles. At evaporation and condensation temperatures of $T_{ev} = 1320 - 1400^\circ$ and $T_c = 1200^\circ$, respectively, the super-saturation α^1 amounts to $10 - 10^3$. We assume the following values for the quantities appearing in equation (1): $\alpha = 2.05 \cdot 10^{-8}$ cm; $M = 52$ g/mole; $\rho = 7.15$ g/cm³; $T = 1300^\circ$ K. The quantity α introduces some uncertainty in the 896 calculation. The value of α for Cr is within the limits of 1000 and 1500 erg/cm. The nucleation rate exceeds 10^{10} nuclei/cm²·sec even at minimum supersaturations ($\alpha = 10$).

Also of interest is another experimental observation that is hard to explain with the mechanism proposed by Sears. During the formation of filamentary

¹ α can be estimated only with order of magnitude accuracy, because a pressure gradient exists in the apparatus. For the same reason the upper limit of α may be somewhat higher.

crystals, generally at first axial growth occurs without any perceptible thickening of the crystal. At a certain time, the rate of axial growth falls off by several orders of magnitude and radial growth commences, causing the crystals to swell. Radial growth is possible only when the nucleation rate on the side faces is rather high. The observation of macrosteps on the faces of filamentary crystals produced in this work and still earlier in references 10 and 11 points to the fact that the growth takes place at high supersaturations. Chernov (ref. 12) has made a detailed study of the processes of formation and displacement of macroscopic steps and also of the dependence of their height on the degree of supersaturation.

These remarks show that the formation and growth of filamentary crystals are far more complicated than they first seemed. The changeover from axial to radial growth with constant controlled process parameters, such as the temperature, stems from a change in the crystal's growth mechanism. This is further confirmed by the fact that thin crystals usually have far fewer growth steps than thick crystals obtained under the same conditions. Moreover, one and the same filamentary crystal can be relatively even in its thin part - near the top - and irregular in its thick part, near the base.

The termination of the axial growth of filamentary crystals at a certain stage of the process can be explained, in principle, by the mechanism of step development on the side faces. Evidently, once a new layer (formed at the base) has reached the top of the crystal in its growth, the feeding of crystallizable substance to the moving end of the whisker comes to an end due to particle diffusion towards the step of the new layer. If many layers exist, practically all of the condensing substance will crystallize near the steps. Hence the speed of radial growth, which is determined by the new layers on the side faces, and

the speed of axial growth, which is determined by a hypothetical screw dislocation at the top, become comparable and the axial growth essentially ceases.

Even if the termination of the axial growth can be described qualitatively, the reason for the difference in the growth mechanisms of thin and thick filamentary crystals and the different structures of their surfaces continue to remain unexplained. If the supersaturation is kept constant during the growth of whiskers, their growth mechanism should not change.

It is difficult to check this assumption experimentally because a number of uncertainties are involved in the determination of the true supersaturation. Even the determination of the supersaturation from the vapor pressure at the measured evaporation and condensation temperatures is associated with large errors. The problem is compounded by the fact that the true and the measured condensation temperatures are not necessarily equal.

In the opinion of several authors, the surface temperature of the growing crystal during condensation, T_c , can exceed the considerably measured temperature of the condensor, T'_c ; this is caused by energy from collisions of particles with the surface and dissipation of the latent heat of crystallization on it. 897 According to an estimate made by Gafner (ref. 13), the difference between T_c and T'_c may amount to hundreds of degrees under certain conditions; this effect decreases as the crystals thicken. If this is correct, then the supersaturation does not remain constant near the surface of the crystals, but increases during their growth.

A certain error in the determination of the supersaturation is related to disregard for the difference between the vapor pressures on macrocrystals (P) and microcrystals (P_∞). According to Thomsen's formula (ref. 15),

$$\ln \frac{P}{P_{\infty}} = \frac{2\sigma M}{pRT r}, \quad (2)$$

where r is the radius of the microcrystal. Crude calculations using equation (2) show, however, that the actual difference between P and P_{∞} is small for chromium.

In considering the tensile strength of needle crystals, one has to bear in mind - as has already been mentioned by Nadgernyy (ref. 14) - that the subjective selection of the crystals for investigation has a very prejudicious effect. For this purpose, the most perfect crystals are usually selected, hence developed the not altogether sound notion of whiskers as almost ideal crystals; generally speaking, this is correct only for single, rather infrequent samples of relatively small cross section.

From the results obtained in our work, it follows that, in spite of the substantial scatter in the observed tensile strengths, there is a persistent tendency for the latter to increase when the sample cross section decreases. High strength is observed in crystals with a uniform surface, as well as in samples exhibiting growth steps (with small dimensions). One can therefore assume that the growth steps on thin crystals do not originate from dislocations. Needle crystals with large cross sections and with ladderlike macrosteps usually have low strength (ref. 7).

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